

FORM PTO-1390

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

EXPRESS MAIL LABEL NO.: EL 132 891 244 US

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: Kinoshita Case 199

U.S. APPLICATION NO.  
(If known, see 37 CFR 1.5): Unknown

INTERNATIONAL APPLICATION NO.: PCT/JP97/01350

INTERNATIONAL FILING DATE: April 18, 1997

PRIORITY DATE CLAIMED: April 19, 1996

TITLE OF INVENTION: FIBER TREATMENT CHEMICALS, FIBER AND PRODUCT  
TREATED WITH THE FIBER TREATMENT CHEMICALS

APPLICANTS FOR DO/EO/US: Masahiro SANO, Takaharu YASUE and Fumioki FUKATSU

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment-document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.  
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:
  1. Formal Drawings (4 sheets)
  2. Japanese Language Article 34 Amendments
  3. Amendment Before First Office Action, including Substitute Specification & Abstract (English translation of Article 34 Amendments)
  4. Form PCT/IB/301 (2 pages)
  5. Form PCT/IB/332 (1 page)
  6. Form PCT/IPEA/409 (3 pages)
  7. Form PCT/RO/101 (Japanese Language) (13 pages)
  8. WIPO document WO97/40227 (26 pages)
  9. Acknowledge postal card.

U.S. APPLICATION NO.  
(If known, see 37 CFR 1.5):  
Unknown

INTERNATIONAL APPLICATION NO.:  
PCT/JP97/01350

ATTORNEY'S DOCKET NUMBER:  
Kinoshita Case 199

17. [X] The following fees are submitted:

**CALCULATIONS** PTO USE ONLY

**BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):**

Search Report has been prepared by the EPO or JPO..... \$ 930.00  
International preliminary examination fee paid to USPTO (37 CFR 1.482)  
..... \$ 720.00  
No international preliminary examination fee paid to USPTO (37 CFR 1.482)  
but international search fee paid to USPTO (37 CFR 1.445(a)(2))..... \$ 790.00  
Neither international preliminary examination fee (37 CFR 1.482) nor  
international search fee (37 CFR 1.445(a)(2)) paid to USPTO..... \$1,070.00  
International preliminary examination fee paid to USPTO (37 CFR 1.482)  
and all claims satisfied provisions of PCT Article 33(2)-(4)..... \$ 98.00

**ENTER APPROPRIATE BASIC FEE AMOUNT** = \$ 930.00

Surcharge of \$130.00 for furnishing the oath or declaration later than [ ] 20 [ ] 30  
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	9 - 20 =	0	X \$ 22.00	\$
Independent claims	4 - 3 =	1	X \$ 82.00	\$ 82.00
MULTIPLE DEPENDENT CLAIMS (if applicable)			+ \$270.00	\$

**TOTAL OF ABOVE CALCULATIONS** = \$ 1,012.00

Reduction by 1/2 for filing by small entity, if applicable. Small Entity Statement  
must also be filed (Note 37 CFR 1.9, 1.27, 1.28).

\$

**SUBTOTAL** = \$ 1,012.00

Processing fee of \$130.00 for furnishing the English translation later than [ ] 20 [ ] 30  
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

**TOTAL NATIONAL FEE** = \$ 1,012.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be  
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property

\$

**TOTAL FEES ENCLOSED** = \$ 1,052.00

**Amount to be refunded  
charged**

\$  
\$

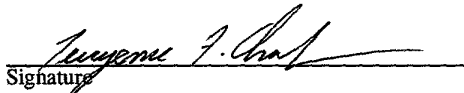
a. [X] A check in the amount of \$ 1,052.00 to cover the above fees is enclosed.

b. [ ] Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees. A duplicate  
copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to  
Deposit Account No. 06-1382. A duplicate copy of this sheet is enclosed.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a)  
or (b)) must be filed and granted to restore the application to pending status.

IN DUPLICATE

  
Signature

SEND ALL CORRESPONDENCE TO:

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Name

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Registration Number

300.9809

405 RECEIVED PTO 16 OCT 1998

PATENT APPLICATION

IN THE U.S. PATENT AND TRADEMARK OFFICE 09/171399  
Express Mail Label No.: EL 132 891 244 US  
October 16, 1998

Applicants : Masahiro SANO et al

For : FIBER TREATMENT CHEMICALS, FIBER AND PRODUCT  
TREATED WITH THE FIBER TREATMENT CHEMICALS

PCT International Application No.: PCT/JP97/01350

PCT International Filing Date : April 18, 1997

U.S. Application No.  
(If known, see 37 C.F.R 1.5) : Unknown

Atty. Docket No.: Kinoshita Case 199

Box PCT  
The Commissioner of Patents and Trademarks  
Washington, D. C. 20231

**PRELIMINARY AMENDMENT CANCELLING CLAIMS**

Sir:

Prior to calculation of the filing fee in the above-identified application, kindly enter the following:

**IN THE CLAIMS**

Please amend Claims 5, 8 and 9 as follows.

Claim 5, line 1; change "any one of claims 3 and 4" to  
---Claim 3---.

Claim 8, line 1; delete "any one of".  
line 2; change "claims from 1 to 7" to  
---Claim 1---.

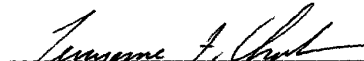
Claim 9, line 1; delete "any one of".  
line 2; change "claims from 1 to 7" to  
---Claim 1---.

REMARKS

This amendment cancels claims to reduce the filing fee.  
Please enter this amendment before calculating the filing fee.

Respectfully submitted,

TFC/smd

  
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Timothy B. Clise	Reg.No. 40 957
Liane L. Churney	Reg.No. 40 694
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Encl: Postal Card

336.9709

IN THE U.S. PATENT AND TRADEMARK OFFICE

Express Mail Label No.: EL 132 891 244 US

October 16, 1998 405 Rec'd PCT/PTO 16 OCT 1998  
09/171399

Applicants : Masahiro SANO et al

For : FIBER TREATMENT CHEMICALS, FIBER AND PRODUCT  
TREATED WITH THE FIBER TREATMENT CHEMICALS

PCT International Application No.: PCT/JP97/01350

PCT International Filing Date : April 18, 1997

U.S. Application No.  
(If known, see 37 C.F.R 1.5) : Unknown

Atty. Docket No.: Kinoshita Case 199

Box PCT  
The Commissioner of Patents and Trademarks  
Washington, D. C. 20231

**AMENDMENT BEFORE FIRST OFFICE ACTION**

Sir:

Prior to issuance of the first Office Action in the above-identified application, kindly enter the following:

**IN THE TITLE**

Please amend the title to read as follows:

---SURFACE TREATMENT CHEMICALS, FIBER AND PRODUCT  
TREATED WITH THE SURFACE TREATMENT CHEMICALS---.

**IN THE ABSTRACT OF THE DISCLOSURE**

Please replace the original Abstract with the Substitute Abstract enclosed herewith.

**IN THE SPECIFICATION**

Please replace the original Specification with the Substitute Specification enclosed herewith.

**IN THE CLAIMS**

Please cancel Claims 1-9 of the originally filed application and replace them with newly presented Claims 10-18 as follows.

10. Surface treatment chemicals, comprising:  
a functional protein obtained by treating protein with  
a cross-linking agent; and  
a solvent-base resin.

11. Surface treatment chemicals, comprising:  
a functional protein obtained by treating protein with  
a cross-linking agent; and  
a water-base resin.

12. Surface treatment chemicals, comprising:  
a water soluble organic substance having an average  
molecular weight of 100 to 20,000; and  
a reactive modifier.

13. The surface treatment chemicals according to Claim 12,  
further comprising chitosan in addition to said water-soluble  
organic substance and said reactive modifier.

14. The surface treatment chemicals according to Claim 12,  
wherein said water soluble organic substance is selected from the  
group consisting of at least one of protein, protein derivatives  
or polysaccharides.

15. The surface treatment chemicals according to Claim 14,  
wherein said protein is selected from the group consisting of at  
least one of fibroin, collagen and wool.

16. Surface treatment chemicals comprising:  
a functional protein obtained by treating protein with  
a cross-linking agent; and  
a reactive modifier.

17. Fibers treated with said surface treatment chemicals  
according to Claim 10.

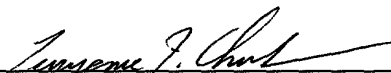
18. Products treated with said surface treatment chemicals according to Claim 10.

REMARKS

The Substitute Abstract and Specification enclosed herewith are the English translations of the originally filed Japanese language Abstract and Specification, including the Article 34 amendments filed at the PCT level. The amendments to the claims include the Article 34 amendments made at the PCT level and delete multiple dependency claims for prosecution in the United States. These amendments are intended to place the application in better form for consideration by the Examiner. Entry of the foregoing amendments prior to issuance of the first Office Action is respectfully solicited.

Respectfully submitted,

TFC/smd

  
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Brian R. Tumm	Reg.No. 36 328

Encl: Substitute Specification and Abstract

336.9709

# **SUBSTITUTE SPECIFICATION AND ABSTRACT**

**(English Translation of Article 34 Amendments  
made at the PCT Level)**



## DESCRIPTION

FIBER TREATMENT CHEMICALS, FIBER AND PRODUCT TREATED  
WITH THE FIBER TREATMENT CHEMICALS

5

## Technical Field

The present invention relates to surface treatment chemicals containing protein or water-soluble organic substances, fibers and textile goods treated with the surface treatment chemicals.

10

## Background Art

Hitherto many techniques have been proposed to impart moisture absorbency to, for instance, polyester synthetic fiber or textile goods made therefrom.

15

For instance, there is a method (1) of treating synthetic fiber with a treating liquid containing acrylic or polyurethane emulsion and finely powdered natural organic substances such as collagen.

20

However, according to above method (1), since the natural organic substance fine powder is merely physically adhered to the synthetic fiber through emulsion as a binder, the fine powder is likely to be dropped off by washing, resulting in inferior durability. Increase of the emulsion ratio to improve the durability hardens touch of the synthetic fiber, thus being less applicable to practical use.

25

There is another method (2) to treat synthetic fibers with a treating liquid containing a modifying agent (monomer) such as polyethylene glycol compounds for improving moisture absorbency.

The method (2) is superior in durability because the modifying agent forms a hydrophilic layer inside and on the synthetic fiber. However, small improvement in moisture absorbency can be observed.

Still another method (3) has been proposed to treat the synthetic fiber with a treating liquid containing a protein aqueous solution and the above  
5 modifying agent. The protein solution is obtained by dissolving, for instance, silk fiber in a calcium chloride solution and dialyzing the solution with a cellophane tube.

The method (3) gives at least an improvement for moisture absorbency due to adherence of protein onto the synthetic fiber but the increase of protein  
10 amount to ensure sufficient moisture absorbency makes hard touch. On the contrary, attempt to maintain the soft touch restricts the protein amount, which makes it impossible to obtain sufficient effect in moisture absorbency.

In addition to the moisture absorbency and the touch described above, improvement in hydrophilic nature, antistatic property, and durability are also  
15 required for fibers and textiles.

### Disclosure of the Invention

A first surface treatment chemicals of the present invention contain functional protein derived by treating protein with a cross-linking agent and a  
20 solvent-base resin.

More specifically, the functional protein is a substance obtained through the following process.

(1) Reacting an aqueous solution containing protein with a cross-linking agent dissolved in an organic solvent, and separately obtaining the  
25 aqueous protein layer containing the cross-linking agent.

(2) Lowering pH of the protein below its isoelectric point by adding acid to the protein solution containing the cross-linking agent and separating precipitate obtained to dry and pulverize.

Any protein substance can be chosen at will for the above protein. For instance, whey, casein, serum-albumin, collagen, gelatin, fibroin, sericin and egg white of a hen, quail, duck, and goose and the like can be used.

For the cross-linking agent, diisocyanate compound, dialdehyde compound, di-keton compound and the like can be used. For the diisocyanate compound, toluene diisocyanate (TDI), diisocyanic-acid diphenylmethane (MDI), isophorone diisocyanate (IPDI), naphthalene diisocyanate (NDI) and the like can be used.

For the solvent to dissolve the cross-linking agent, chloroform, hexane, toluene and the like can be used.

For the acid, acetic acid, citric acid, succinic acid, lactic acid, tartaric acid, and fumaric acid and the like can be used.

The solvent-base resins are urethane resin, acrylic resin or vinyl chloride resin and others dissolved in solvents including at least one of dimethylformamide (DMF), methylethylketone (MEK), toluene, cyclohexane, and butyl acetate and the like.

The functional protein derived through the above described process is soluble in organic solvents and insoluble in water.

The surface treatment chemicals in the present invention can be prepared by dissolving the functional protein and mixing the solution with the solvent-base resin .

The dissolution of the functional protein can be carried out by dispersing a protein powder in an organic solvent (such as DMF) at room

temperature, stirring and completely dissolving the protein powder until the liquid becomes transparent through heating to 60°C to 80°C and then cooling to room temperature.

The mixing with the solvent-base resin is carried out by adding the functional protein solution little by little to the solvent-base resin solution while stirring.

The content of the functional protein is from 0.1 wt% to 50 wt% , preferably from 1 wt% to 30 wt%. When the content is less than 0.1 wt%, sufficient effect can not be obtained, while the content is increased to more than 50 wt%, the treating chemicals are apt to be peeled off and the transparency of the fiber may be lowered.

Since the surface treatment chemicals of the present invention have a mixture of the functional protein with solvent-base resin in a molecular level, touch, hygroscopic-nonhygroscopic property, durability and transparency can be improved without degradation of the resin characteristics.

Second surface treatment chemicals of the present invention contain functional protein derived by treating the protein with a cross-linking agent and a water-base resin.

More specifically, the functional protein of the second treatment chemical is derived from the following process.

(1) Reacting an aqueous solution containing protein with a cross-linking agent dissolved in an organic solvent, and separately obtaining the aqueous protein layer containing the cross-linking agent.

(2) Raising pH of the protein solution above the protein's isoelectric point and separating modified protein to dry and pulverize.

Any protein substance can be chosen at will for the above protein. For

instance, whey, casein, serum-albumin, collagen, gelatin, fibroin, sericin and egg white of a hen, quail, duck, and goose and the like can be used.

For the cross-linking agent, diisocyanate compounds, dialdehyde compounds, diketone compounds and the like can be used. For the  
5 diisocyanate compounds, toluen diisocyanate (TDI), diisocyanic-acid diphenylmethane (MDI), isophorone diisocyanate (IPDI), and naphthalene diisocyanate (NDI) and the like can be used.

For the solvent to dissolve the cross-linking agent, chloroform, hexane, toluene and the like can be used.

10 The water-base resins refer to resins whose solvent is water and include emulsions and water soluble resins. Emulsions of silicon group, acryl group, urethane group, vinyl acetate group and vinyl chloride group and the like are included in the emulsion. The water soluble resins include polyvinyl alcohol, high polymer cellulose, polyethylene imine, and polyethylene oxide.

15 The functional protein thus obtained is water soluble but becomes insoluble after heat set.

The surface treatment chemicals of the present invention can be prepared by dissolving the functional protein, and then mixing the solution with a water-base resin.

20 The functional protein is dissolved by dispersing a protein powder in water at room temperature, stirring and heating up the dispersions to 60°C to 80°C until the liquid becomes transparent to dissolve the protein completely, and then the solution is cooled to room temperature.

The mixing with the water-base resin is done by adding the functional  
25 protein solution to the water-base resin in appropriate proportion.

The content of the functional protein is from 0.1 wt% to 50 wt%,

preferably from 1 wt% to 30 wt%. When the content is less than 0.1 wt%, sufficient effect can not be obtained, while the content is increased to more than 50 wt%, the fiber treating chemicals are apt to be peeled off or the transparency of the fiber may be lowered.

5 Third surface treatment chemicals of the present invention contain water soluble organic substances having average molecular weight of 100 to 20000 and a reactive modifier.

The water soluble organic substances include water soluble natural organic substances and derivatives which are derived from decomposition and  
10 modification of the above-described organic substance as a base material.

The water soluble organic substances of which molecular weight is less than 100 are poor in durability. On the contrary, when the molecular weight of the water soluble organic substance exceeds 20000 and at the same time the content is increased so much as to obtain sufficient functions, the fiber touch  
15 becomes hard.

Adjustment of average molecular weight can be conducted by chemical means such as hydrolytic degradation with well-used acid or alkali.

It is believed that when the fiber is treated with the surface treatment chemicals, the soluble organic substance and the reactive modifier are  
20 polymerized by the application of heat and form a durable hydrophilic layer on the surface of and in the fiber.

The soluble organic substance can be protein or a protein derivative.

The protein derivatives can be obtained by decomposing or modifying the protein as a base material.

25 Concrete examples of the protein are fibroin, collagen, wool and combinations thereof.

For the protein, it is preferable to use the fibroin considering availability and price. However, the protein is not limited to the specific examples and other protein such as egg white, whey, and the like can also be used.

5 For the reactive modifier, for instance, (1) hydrophilic compounds having a polymerizable vinyl group in the molecule (2) a monomer containing any one of hydroxyl group, carboxyl group, amino group, sulfonic group, and phosphate group, (3) hydrophilic compounds having a epoxy group, and (4) compounds having a aziridine group can be used.

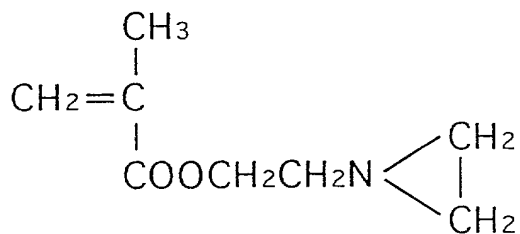
10 The concrete examples of the above (1) are polyethyleneglycol diacrylate, polyethylene glycol dimetacrylate, bisphenol-A polyethyleneglycol diacrylate, bisphenol-A polyethyleneglycol di-metacrylate, bisphenol-S polyethyleneglycol dimetacrylate and the like.

15 The concrete examples of the above (2) are acrylic acid, metacrylic acid, maleic acid, itaconic acid, acryl amide, metacryl amide, vinyl sulfonic acid, hydroxypropyl metacrylate and the like.

The concrete examples of the above (3) are polyethyleneglycol diglycidyl ether and the like.

20 The concrete examples of the above (4) are compounds having the following chemical formula 1 and the like.

(Chemical formula 1)



25

In the third surface treatment chemicals, chitosan can be used in addition to the water soluble organic substance and the reactive modifier.

As for the chitosan, it is not necessary to limit to be of the average molecular weight from 100 to 20000.

5 By adding chitosan to the third surface treatment chemicals, an improvement in moisture absorbency can be achieved.

Fourth surface treatment chemicals contain a functional protein obtained by treating protein with a cross-linking agent and a reactive modifier.

10 The functional protein relating to the fourth surface treatment chemicals is the same functional protein of the second surface treatment chemicals.

The reactive modifier of the fourth surface treatment chemicals is the same reactive modifier in the third surface treatment chemicals.

The fiber in the present invention is treated with any one of the first to the fourth surface treatment chemicals.

15 Well known synthetic fibers such as nylon, polyester, polyurethane and the like are included in the above described fibers.

The products of the present invention are treated with any one of the first to the fourth surface treatment chemicals.

20 The products include thread, textile, knitting and non-woven fabric made of the synthetic fiber described above. Cotton, wool, and hemp may be combined. The concrete products are blouses, dress shirts, pants, skirts, cloth backings, and cover materials for furniture such as a chair.

The treatment method of the surface treatment chemicals is optional and can be, for instance, a dipping method or a padding method.

25 The dipping method includes leaving-in-room-temperature method (Shitsuon-seiti-hou in Japanese) and heat-and-stir method (Kanetsu-kakuhan-



hou in Japanese).

The padding method includes pad-dry method and pad-steam method, however, the pad-steam method is preferable.

In the case of the fiber products, the protein becomes insoluble in water after the chemicals are heat-set, and the protein does not fall out even by repeated washing. The fiber products thus treated are so superior in durability that good feeling of touch, moisture absorbency, water vapor permeability, and transparency are still maintained even after a long period of use.

Products other than the fiber products are film, sheet and leather and the like.

The leather includes vinyl leather, synthetic leather, artificial leather, split leather and resin coated cloth.

As a method for treating a surface of film, sheet, and leather, a method of spray coating, gravure coating, or knife coating, etc. can be used.

The finished surface layer of the product formed by the surface treatment chemicals gives a good surface smoothness and a comfortable touch. And the layer is so superior in transparency that print patterns on cloth, and transparency of transparent film or leather are not spoiled.

A film made from the surface treatment chemicals may be prepared in advance and a finished surface layer may be formed by affixing the film on a surface of a product.

#### Brief Description of Drawings

Fig. 1 is a measurement result with FTIR for the functional protein obtained in experiment 4;

Fig. 2 is a measurement result with FTIR for a pair of the panty hose of

experiment 6, after washing 10 times;

Fig. 3 is a measurement result with FTIR for a pair of the panty hose in comparison 14; and

Fig. 4 is a measurement result with FTIR for a pair of the panty hose in comparison 15 after washing 5 times.

### Best Mode for Carrying out the Invention

#### (A first embodiment)

Surface treatment chemicals of the present embodiment correspond to a previously described first surface treatment chemicals, which are prepared as follows.

First, a functional protein is prepared as follows.

An aqueous solution containing protein and a cross-linking agent dissolved in an organic solvent are allowed to react and an aqueous layer of the protein solution containing the cross-linking agent is separately obtained.

Then acid is added to the protein solution containing the cross-linking agent to lower the pH below the isoelectric point of the protein. A precipitate thus derived is isolated and dried to obtain a powder of the functional protein.

The powder of the functional protein thus obtained is dispersed in an organic solvent at room temperature and the dispersions is stirred and heated up to 60°C to 80°C thereby completely dissolving the protein until the solution becomes transparent. Then the solution is cooled to room temperature.

The functional protein solution is mixed with a solvent-base resin by adding the solution gradually to the resin while stirring to obtain the surface treatment chemicals relating to the present embodiment.

A finished surface layer is formed by treating surface of a leather or the

like with the surface treatment chemicals.

Alternatively, a film may be prepared in advance using the treatment chemicals and a finished surface layer can be made by affixing the film on a surface of a product.

5 (Experiment 1)

A powder of whey protein was diluted with water to make a 3.5% protein solution, and the pH of the solution was adjusted to 12 with sodium hydroxide. A chloroform solution of 2,4-toluene diisocyanate (TDI) was added to the protein solution and allowed to react at 45°C for two hours. After  
10 the reaction, the reacted liquid separates into a water layer and a chloroform layer while leaving at rest at room temperature for two hours. The water layer was separately obtained, eliminating the chloroform layer by filtering. The pH of the water layer thus obtained was adjusted to 3.5 to precipitate a cross-linked protein. The precipitated protein was filtered and freeze-dried to obtain  
15 a powder of the functional protein.

Next, 150g of the functional protein powder thus obtained was put into dimethylformamide (DMF) while stirring at room temperature to make dispersions.

The dispersions were stirred for 15 minutes in a hot water bath at a  
20 temperature of 80°C to make the powder of the functional protein completely dissolve. The liquid was then spontaneously cooled to room temperature to obtain the functional protein solution. Content of the functional protein in the solution was 15 wt%.

For a solvent-base resin, a urethane resin solved in DMF ("CRISVON  
25 S-750 (trade name) made by Dainippon Ink and Chemicals Inc.) was used. The functional protein solution was slowly added to the solvent-base resin

solution to mix with each other while stirring and a solution of the surface treatment chemicals of the present embodiment was obtained. The content of the functional protein was 10wt% of all solid state surface treatment chemicals.

After a pattern paper was coated with the solution of the surface treatment chemicals with a bar coater and dried at 80°C, a film of 20μm in thickness was made.

(Comparison 1)

A resin solution without the functional protein was prepared by adding only DMF to a solvent-base resin so that the solid state resin content was 20%. Using the resin solution, a film of 20μm in thickness was prepared in the same way as in the experiment 1.

(Comparison 2)

An insoluble collagen powder (average particle size was 5μm) which was obtained by mechanically pulverizing shaved chipping of cowhide, was used instead of the functional protein in experiment 1 and a solution having 10 wt% of the collagen powder in all dry solid matter was obtained.

Using the solution, a film of 20μm in thickness was prepared in the same way as in the experiment 1.

(Experiment 2)

“Luck skin U-65 “(trade name, manufactured by SEIKOH CHEMICALS Co., Ltd.) was used for the urethane resin in experiment 1, and with the other conditions being the same as in the experiment 1, a solution of the surface treatment chemicals of the present embodiment was obtained.

Then, using the solution of the surface treatment chemicals for a surface treatment agent, a finished surface layer was made by coating on a vinylchloride leather sheet used for a pocketbook cover with a gravure coater.

The coating amount of the solution was 20g/m<sup>2</sup>.

(Comparison 3)

In the condition of experiment 2, a solution without the functional protein was prepared.

5 Then using the solution thus obtained, a finished surface layer was made by coating on vinylchloride leather in the same way as in experiment 2.

(Comparison 4)

10 An insoluble collagen powder (average particle size was 5μm) which was obtained by mechanically pulverizing shaved chipping of cowhide, was used instead of the functional protein in experiment 2 and a solution having 10 wt% of the collagen powder in all dry solid matter was obtained.

Then using the solution thus obtained, a finished surface layer was made by coating on vinylchloride leather in the same way as in experiment 2.

(Experiment 3)

15 Using "Luck skin U-65" (trade name, manufactured by Seiko Chemical Co. Ltd.) for the urethane resin in experiment 1, and with the same condition as in experiment 1 for other conditions, a solution of the surface treatment chemicals of the present embodiment was obtained.

20 Then, using the solution of the surface treatment chemicals, a finished surface layer was made by coating on an enameled vinylchloride leather sheet for a bag with a gravure coater. The coating amount of the solution was 20g/m<sup>2</sup>.

(Comparison 5)

25 Using the same process as in experiment 3, a solution without the functional protein was prepared.

Using the solution thus obtained, a finished surface layer was made by

coating on enameled vinylchloride leather in the same way as in experiment 3.  
(Comparison 6)

A collagen powder was used instead of the functional protein in experiment 3 and a solution having 10 wt% of the collagen powder in all solids  
5 constituents was obtained.

Then, using the solution thus obtained, a finished surface layer was made by coating on enameled vinylchloride leather in the same way as in experiment 3.

(Comparison 7)

10 Enameled vinylchloride leather use was taken as the present comparison for evaluation.

(Evaluation of characteristics)

At least one of characteristics among moisture permeability, tensile strength, and degree of elongation was measured and at least one of  
15 characteristics between surface touch and glossiness was evaluated with regard to each of experiments from 1 to 3 and the comparisons from 1 to 7. Utility tests A and B are also carried out and the results were evaluated. Tables 1 to 3 show the results of these evaluations.

The moisture permeability is measured in conformity with JIS L 1099-  
20 A.

The tensile strength and degree of elongation measurements are based on JIS K-7311.

For evaluating surface touch, 20 people touch the surface of test samples and evaluate the touch based on a criteria written below and the  
25 average of the evaluation by these people is taken as a result of the evaluation.

The glossiness is measured based on a method of specular reflection at

an angle of 60 degrees of JIS K-7105.

5 point ... excellent touch.

4 point ... good touch.

3 point ... normal.

5 2 point... poor touch.

1 point ... bad touch.

The utility test A was carried out by preparing a pocketbook using the leather obtained from the experiment and checking the change at the bent portion of the leather cover.

10 The utility test B was performed in such a way that the leather obtained is sewed on a machine and easiness of sewing is evaluated with reference to the criterion written below by 10 people randomly selected. The result of the evaluation is an average of the points by the 10 people.

5 point ... good smoothness, very easy to machine

15 4 point... adequate smoothness, easy to machine.

3 point ... normal.

2 point ... a little tackiness, hard to machine.

1 point ... a lot of tackiness, very hard to machine.

20 (Table 1)

	Permeability	tensile strength	elongation	touch
Experiment 1	1900g/m <sup>2</sup> /24h	580kg/cm <sup>2</sup>	420%	4.2
Comparison 1	1350g/m <sup>2</sup> /24h	600kg/cm <sup>2</sup>	400%	1.6
Comparison 2	1920g/m <sup>2</sup> /24h	390kg/cm <sup>2</sup>	300%	4.3

In table 1, it is observed that the results in tensile strength and

elongation are good. And the results in permeability and touch are also good, since the film in experiment 1 contains the functional protein.

On the contrary, since the film in comparison 1 does not contain the functional protein, though the results in tensile strength and elongation are good, the results in permeability and touch are inferior to the film by experiment 1.

Since the film of comparison 2 contains collagen powder instead of the functional protein, the results in tensile strength and elongation are inferior to the film by experiment 1, though the results in permeability and touch are good.

(Table 2)

	touch	utility test A
Experiment 2	4.4	no defective
Comparison 3	2.6	no defective
Comparison 4	4.2	blanching on bent portion

From table 2, it is understood that the result in evaluation of touch is good, since the vinylchloride leather of experiment 2 contains the functional protein in the surface layer. The result in the utility test shows no abnormality, having high durability.

On the contrary, since the vinylchloride leather of comparison 3 does not contain the functional protein in the finished surface layer, the touch is poor, though the utility test shows no abnormality.

Since the vinylchloride leather in comparison 4 contains an insoluble collagen powder instead of the functional protein in the finished surface layer, blanching at the bent portion is appeared, showing that the surface layer



obtained by comparison 4 is defective though touch is good.

(Table 3)

	touch	utility test B	Glossiness
Experiment 3	4.2	4.8	87.2%
Comparison 5	2.8	2.0	88.4%
Comparison 6	4.3	4.2	62.3%
Comparison 7	2.6	1.5	89.8%

5 From table 3, it is observed that the touch and glossiness test show good results, because the functional protein is contained in the finished surface layer of the enameled vinylchloride leather of experiment 3. And good smoothness and easy handling in sewing is also shown.

10 On the contrary, as the enameled vinylchloride leather of comparison 5 does not contain the functional protein in the finished surface layer, both touch and utility test B show unfavorable results.

15 As the enameled vinylchloride leather of comparison 6 contains the collagen powder instead of the functional protein in the finished surface layer, the leather is inferior in glossiness though the results of the touch test and utility test are good.

Since the leather of comparison 7 is enameled vinylchloride leather without a finished surface layer, it has good glossiness but has very bad results in touch and utility test.

(A second embodiment)

20 The surface treatment chemicals of the second embodiment correspond to the previously described second surface treatment chemicals and can be

prepared as follows.

First, a functional protein is prepared as follows.

An aqueous protein solution and a cross-linking agent dissolved in an organic solvent are allowed to react with each other and an aqueous layer of protein solution containing the cross-linking agent is separately obtained. 5 Incidentally, it is preferable that the protein is pretreated in advance, by conducting hydrolysis or the like, to improve water solubility.

Then, pH of the protein solution containing the cross-linking agent is adjusted to a pH value more than the isoelectric point of protein. After the adjustment, the modified protein is separated, and dried to obtain a powder of the functional protein. 10

Secondly, the obtained protein powder is dispersed in water at room temperature, and the dispersions are heated, for instance, up to 60° to 80°C while stirring until the liquid becomes transparent so that the powder is completely dissolved, and then the solution is cooled to room temperature. 15

The surface treatment chemicals of the present embodiment can be obtained by mixing the functional protein solution with a water-base resin at adequate proportions.

A surface treated layer of film, sheet, leather, knitting, textiles or non woven fabric is formed by treating surface thereof with the surface treatment chemicals. 20

(Experiment 4)

A powder of whey protein was diluted with water to make a 3.5% protein solution and the solution was adjusted by sodium hydroxide to pH 12. 25 A chloroform solution of 2,4-toluen diisocyanate (TDI) was added to the protein solution and kept for 2 hours at 45°C for allowing to react with each

other. After the reaction, the liquid was kept for 2 hours at room temperature. Then, a water layer and a chloroform layer were separated. The water layer was filtered to be separated from the chloroform layer. The pH of the water layer was adjusted to 7 and a functional protein powder was obtained after drying.

Then 50g of the functional protein powder was dispersed in 950g of water. The dispersions were kept in a hot water bath at a temperature of 80°C for 20 minutes while stirring to completely dissolve the protein powder. Thus, 5 wt% of the protein solution was obtained. After the solution was naturally cooled, 82g of the solution was mixed with 100g of acryl type emulsion (Yodosol 2D540 (trade name) Kanebo N.S.C. Co. Ltd.), and uniformly blended with a propeller stirrer to make a solution of surface treatment chemicals.

The surface treatment solution was coated on a transparent polyvinylchloride sheet at a coating amount of 10g/m<sup>2</sup> with a gravure coater and dried at a temperature of 120°C to obtain a sheet having a finished surface layer.

(Comparison 8)

Instead of the functional protein used in the experiment, an insoluble collagen powder (average particle size 5μm) derived from mechanically pulverized chipping of shaved cowhide was used. The collagen powder was mixed to acryl type emulsion (Yodosol 2D540 (trade name) Kanebo N. S. C. Co. Ltd.), so that the content ratio of the collagen powder to the total solid matter (the collagen powder and the resin solid) reached 10 wt% to obtain a solution of the surface treatment chemicals.

Then, after the solution of the surface treatment chemicals was coated

on a polyvinylchloride sheet in the same way as in the experiment 4, a sheet having a finished surface layer was obtained by drying the coated sheet.

(Comparison 9)

5 Instead of the functional protein used in experiment 4, a soluble gelatin was used (an average molecular weight was 3000). The soluble gelatin was mixed to an acryl type emulsion to obtain a solution of surface treatment chemicals.

10 Then, after the solution of surface treatment chemicals was coated on a polyvinylchloride sheet in the same way as in experiment 4, a sheet having a finished surface layer was obtained by drying the coated sheet.

(Comparison 10)

15 The acryl type emulsion (Yodosol 2D540 (trade name)) containing no protein was coated on a polyvinylchloride sheet in the same way as in experiment 4, and a sheet having a finished surface layer was obtained by drying the coated sheet.

(Experiment 5)

20 The sheet having a finished surface layer, which was obtained from the same process as in experiment 4, was laminated on enameled polyvinyl chloride leather by using an adhesive agent to obtain enameled polyvinyl chloride leather having a finished surface layer.

(Comparison 11)

Enameled vinylchloride leather for evaluation was taken as the present comparison.

(Evaluation of characteristics)

25 The samples obtained in experiment 4 and comparisons 8 to 10 were checked in view of surface touch, antifouling property (water resistance), and

transparency. The samples obtained in experiment 5 and comparison 11 were measured in glossiness and evaluated in utility. Table 4 shows the results.

For the evaluation of the surface touch, 20 people touched the surface of test samples and evaluate the feeling of touch based on the criteria written below and the average of the evaluation points by the twenty people was taken as the result of the evaluation.

5 point ... excellent surface touch.

4 point ... good surface touch.

3 point ... normal.

10 2 point ... poor surface touch.

1 point ... worse surface touch.

The antifouling property (water resistance) was measured as follows. A drop of water, soy sauce and a kitchen detergent (the concentration was 1g/1000ml) was dropped on the test samples. After 24 hours, the dropped spots were wiped off with a dried cloth and the surface conditions were evaluated by observation.

The transparency was evaluated by judging with the naked eye.

The glossiness evaluation was carried out based on the method of specular reflection at an angle of 60 degrees in JIS K 7105.

20 The utility test was performed in such a way that the leather obtained was sewed on a machine and the easiness of sewing was evaluated with reference to the criterion below by 10 people randomly selected. The result of the evaluation is an average of the evaluation points by the 10 people.

5 point ... good smoothness, very easy to machine.

25 4 point ... adequate smoothness, easy to machine.

3 point ... normal.

2 point... a little tackiness, hard to machine.

1 point ... lot of tackiness, very hard to machine.

(Table 4)

	Surface Touch	utility test	antifouling			trans- parency	gloss- ness
			water	soy sauce	detergent		
Experi ment 4	4.1	—	normal	normal	normal	trans parent	—
Compar ison 8	4.2	—	normal	normal	normal	foggy	—
Compar ison 9	3.9	—	① slimy	② tinting	① slimy	trans parent	—
Compar ison 10	2.0	—	normal	normal	normal	trans parent	—
Experi ment 5	4.3	4.6	—	—	—	—	85.6%
Compar ison 11	1.5	1.5	—	—	—	—	89.8%

5 ①Slime occurs on the surface.

②The color of soy sauce remains after wiping off.

As the polyvinyl chloride sheet of experiment 4 contains the functional protein in the finished surface layer, it is clear from table 4 that surface touch,  
10 antifouling property, and transparency are all good. Therefore the polyvinyl chloride sheet is suitable for a table cloth, for instance.

Since the polyvinyl chloride sheet of comparison 8 contains an

insoluble collagen powder as a protein in the finished surface layer, as for transparency, a frosted glass like fogging appears and the sheet looks unattractive, though surface touch and antifouling property show no problem.

5 Since the polyvinyl chloride sheet in comparison 9 has a soluble gelatin as a protein in the finished surface layer, though it has no problem in surface touch and transparency, but has a problem in antifouling property. And has also a problem in terms of practical use because the soluble gelatin is eluted out when contacted with water.

10 Since the polyvinyl chloride sheet of comparison 10 does not contain any protein in the finished surface layer, the result in surface touch is defective, though it has no problem in antifouling property and transparency.

15 As the enameled polyvinyl chloride leather in experiment 5 contains the functional protein in the finished surface layer, it is observed that the results on surface touch and glossiness are good. And the utility test is also good due to the excellent easiness in sewing.

On the contrary, since the enameled polyvinyl chloride leather sheet of comparison 11 does not contain any protein in the finished surface, it is inferior in surface touch, though it is superior in glossiness. And it is very hard to sew on a machine, so the result on the utility test is poor.

20 (Experiment 6)

4% by weight of a solution having 5 wt% of the functional protein solution obtained in experiment 4, 2% by weight of urethane type emulsion (UN - 11 (trade name) made by KYOEISHA CHEMICAL Co., Ltd.), 94% by weight of water were put in a drum type dyeing machine.

25 Dyed panty hose were put into the dyeing machine at a bath ratio of 1 : 20 and kept immersed for 15 minutes at 40°C and the absorbed water was

removed with a centrifugal dehydrator at a pick up rate of 30 %. Then, by heat setting the panty hose with a steam drier, panty hose on the surface of which the protein was firmly fixed were obtained.

(Comparison 12)

5       Panty hose on the market having the same yarn configuration as that used in experiment 6 were taken as the comparison 12.

(Comparison 13)

The dyed panty hose which were used in experiment 6 were used for comparison 13.

10   (Comparison 14)

Similar to experiment 6 but not using protein, 2% by weight of the urethane type emulsion (UN-11 (trade name)) and 98% by weight of water were put into the drum type dyeing machine.

Panty hose were processed with the same condition as that in  
15   experiment 6.

(Comparison 15)

Using soluble fibroin (average molecular weight 4800) instead of the functional protein in experiment 6, the panty hose firmly fixed with fibroin on the fiber surface were obtained through the same process as in experiment 6.

20   (Evaluation of characteristics)

Water absorbency and surface touch of the panty hose in experiment 6 and comparisons from 12 to 15 were evaluated and each frictional electrification voltage was measured. These results are shown in Table 5. The panty hose in experiment 6 and comparisons from 14 to 15 were checked in  
25   view of adhering condition of protein. These results are shown in Fig. 2 to Fig. 4.



The water absorbency measurement was performed based on JIS L 1096-A.

The test method for surface touch was the same as the method in experiment 1.

5 The frictional electrification voltage was measured in compliance with JIS L 1094-B.

To evaluate the fixing condition of protein, the panty hose were violently stirred in 1 liter of water at 40°C for 24 hours and the adherents are forcibly extracted and dried. The solid residue is measured with FTIR (Fourier  
10 Transform Infrared Spectrometer).

For the evaluation of the experiment 6, the panty hose obtained in the experiment 6 are washed 10 times and the panty hose in comparison 15 are washed 5 times, then protein adhesion is measured. Incidentally, one washing is counted by washing the panty hose by using a monolayer full-  
15 automatic home washer with home laundry detergent (Monogen uni (trade name) P & G Co. Ltd.) at the concentration of 2g/liter for 5 minutes, rinsing 2 times, and dewatering for 4 minutes. The panty hose are put in a wash-net during the washing.

The FTIR measurement result of the dried sample of the functional  
20 protein 5 wt% solution obtained in experiment 4 is shown in Fig. 1. According to Fig. 1, peaks of protein caused by amide bond are found at around 1550cm<sup>-1</sup> and 1650cm<sup>-1</sup>.

(Table 5)

	Surface touch	water absorbing speed	frictional electrification voltage (V)
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Experiment 6	4.2	less than 1 sec.	1200
Comparison 12	3.6	more than 5 min.	3800
Comparison 13	3.0	more than 5 min.	2400
Comparison 14	3.2	more than 5 min.	4300
Comparison 15	3.4	10 sec.	1600

From table 5, it is understood that the panty hose have good surface touch and also good water absorbency, since the panty hose of experiment 6 have the functional protein fixed on the fiber surface. The panty hose quickly absorb sweat, rapidly canceling musty feelings. They have also good antistatic property. These effects are also obtained when the finished surface layer containing the functional protein is formed on a polyester cloth and the like.

From the result of FTIR measurement shown in Fig. 2, peaks caused by protein can be seen at around  $1550\text{ cm}^{-1}$  and  $1650\text{ cm}^{-1}$ , which shows that the functional protein remains on the fiber surface without being washed out even after 10 times of washing.

Since the panty hose in comparison 12 and 13 are commercially available and no protein on the fiber surface, they are so poor in water absorbency that they can not quickly absorb sweat and keeps musty feelings. And they are inferior in antistatic property, though they are normal in surface touch.

Since the panty hose of comparison 14 have no protein on the fiber surface, they are found to be inferior in water absorbency and antistatic property.

Since the panty hose of comparison 15 have soluble fibroin as a protein, it is found in table 5 that they are superior in surface touch, water

absorbency and antistatic property. But as shown in Fig 4, there is no peak characteristic of protein, which shows that the soluble fibroin was flown out of the fiber surface after 5 washes.

(A third embodiment)

5 Surface treatment chemicals of the third embodiment correspond to the third surface treatment chemicals, having the following constituents and solvents.

	Soluble organic substance	··· ··· 1 to 15 wt%
	reactive modifier	··· ··· 0.1 to 10 wt%
10	others	··· ··· 0 to 10 wt%

As the solvent, water, alcohol, dimethyl formamide, acetone, dimethyl sulfoxide or a mixture thereof can be used.

A polymerization initiator, a carrier for the reactive modifier and others may be added as necessary as other constituents.

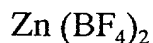
15 The polymerization initiator includes peroxides, azo compounds, and metal salts.

The carrier is to help the reactive modifier penetrate deep inside fiber from the surface layer. The concrete examples of the carrier are chlorobenzenes, methyl naphthalenes, diphenyls, aromatic esters, and aliphatic  
20 halogenated hydrocarbons and so on.

(Experiment 7)

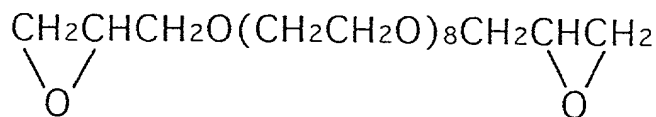
In the third embodiment, a concrete example of constituents of the surface treatment chemicals and each concentration were as follows.

	a hydrolytic degradation product of silk fibroin	····· 5 wt%
25	a compound having the chemical formula 2	····· 5 wt%
	water	····· 89 wt%



..... 1 wt%

(Chemical formula 2)



5

The silk fibroin hydrolytic degradation product of experiment 7 was obtained as follows.

Silk fibroin yarn from which sericin was removed by ordinary method was dissolved in 2N-HCl solution at 70°C for 1 hour. Then the solution was  
10 neutralized with caustic soda to obtain the hydrolytic degradation product solution of fibroin. A fibroin powder was obtained by spray drying the fibroin solution. The fibroin powder had a molecular weight of about 4800 and shows water solubility.

Taffeta cloth made from 100% polyester (Meduke [Japanese unit  
15 showing weight of a textile for predetermined area] 120g/m<sup>3</sup>) was impregnated in the surface treatment chemicals and was wrung to impregnation rate 70% with a mangle. The cloth was treated with heated moisture at 105°C for 10 minutes and put into a water bath at 40°C for 10 minutes. Then the cloth was dried and treated to heat set.

20 (Experiment 8)

In the third embodiment, a concrete example of each constituent of the surface treatment chemicals and their concentration were as follows.

Hydrolytic degradation product of silk fibroin..... 2 wt%

collagen ..... 3 wt%

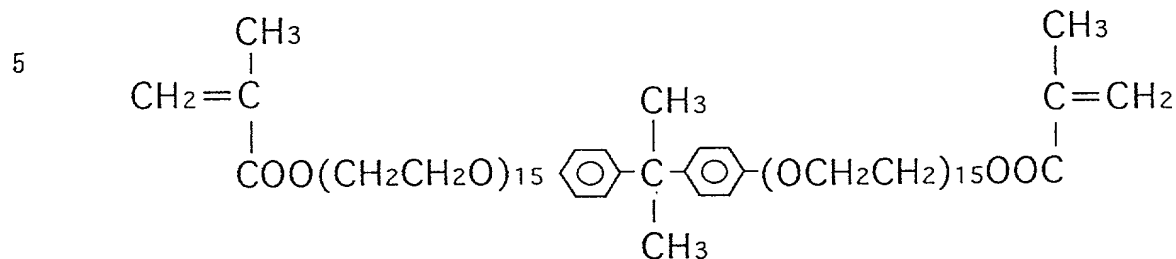
25 a compound having the chemical formula 1 ..... 2 wt%

a compound having the chemical formula 3 ..... 4 wt%

water ..... 88.5 wt%

$(\text{NH}_4)_2\text{S}_2\text{O}_8$  ..... 0.5 wt%

(Chemical formula 3)



10 As the collagen, NUTRILAN (trade name, manufactured by HENKEL HAKUSUI) which was a powder having an average molecular weight of about 1500 was used.

The treatment on taffeta cloth with the surface treatment chemicals was carried out in the same way as in experiment 1.

15 (Experiment 9)

In the above embodiment, a concrete example of each constituent of the surface treatment chemicals and their concentration were as follows.

Hydrolytic degradation product of silk fibroin ..... 4 wt%

a compound having the chemical formula 3 ..... 2 wt%

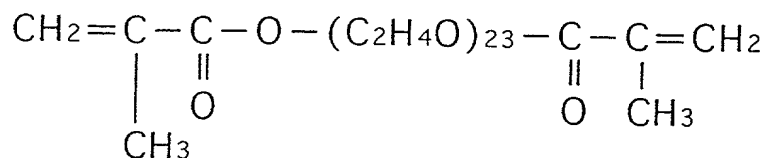
20 a compound having the chemical formula 4 ..... 4 wt%

water ..... 39.5 wt%

$(\text{NH}_4)_2\text{S}_2\text{O}_8$  ..... 0.5 wt%

chitosan 1% aqueous solution ..... 50 wt%

(Chemical formula 4)



5

As the chitosan, CTA-1 lactic acid (trade name, Kataoka Chikarin Co.,Ltd.) having an average molecular weight of about 300, 000 was used.

The treatment on taffeta cloth with the surface treatment chemicals was carried out in the same way as in experiment 7.

10 (Comparison 16)

The amount of the hydrolytic degradation product of silk fibroin in the surface treatment chemicals of experiment 7 was set to 0 and the amount of water was changed to 94 wt%. Other constituents and their concentrations were the same as in experiment 7.

15 The treatment on the taffeta cloth with the surface treatment chemicals was carried out in the same way as in experiment 7. (Comparison 17).

20 The amount of the hydrolytic degradation product of silk fibroin and collagen in the surface treatment chemicals of experiment 8 were set to 0 and the amount of water was changed to 93.5 wt%. Other constituents and their concentrations were the same as in experiment 7.

The treatment on the taffeta cloth with the surface treatment chemicals was carried out in the same way as in experiment 7. (Comparison 18)

25 The amount of the hydrolytic degradation product of silk fibroin and chitosan in the surface treatment chemicals of experiment 9 were set to 0 and

the amount of water was changed to 93.5wt%. Other constituents and their concentrations were the same as in experiment 8.

The treatment on the taffeta cloth with the surface treatment chemicals was carried out in the same way as in experiment 7.

5 (Comparison 19)

Silk fibroin having a high molecular weight was used instead of the hydrolytic degradation product of silk fibroin in the surface treatment chemicals of experiment 7. Other constituents and their concentrations were the same as in experiment 7. Silk fibroin having a high molecular weight in  
10 this comparison was obtained from the following process.

Silk fibroin yarn from which sericin was removed by a common method was heated to be dissolved in 50 wt% aqueous solution of calcium chloride and the solution thus obtained was dialyzed and desalted through a cellulose tube. The concentration of fibroin in the fibroin solution thus obtained was 4.2 wt%.  
15 The molecular weight of fibroin in the solution was about 100,000. Incidentally, since the solution is unstable (tends to gel in a few days), it was used within the day of preparation.

The treatment on the taffeta cloth with the surface treatment chemicals was carried out in the same way as in experiment 7.

20 (Comparison 20)

Untreated polyester cloth without any treatment with surface treatment chemicals was used as comparison 20.

(Evaluation of characteristics)

Moisture absorbency at the start and after washing and frictional  
25 electrification voltage of the treated taffeta cloth obtained by the process in experiments from 7 to 9 and comparisons from 16 to 20 were measured. And

also feeling of the cloth was evaluated. These results are shown in tables 6 and 7.

The moisture absorbency was measured by: leaving samples of treated taffeta cloth for 12 hours in an atmosphere of 23°C, 30%RH to condition moisture, transferring to a place having an atmosphere of 30°C, 80% RH, and measuring change in weight.

The washing was carried out based on JIS L-0217 method 103.

The measurement of the frictional electrification voltage was performed in compliance with JIS L-1094 method B.

The feeling of the cloth was evaluated by randomly gathered 20 people to touch the samples and evaluate based on the criterion written below, on the assumption that the samples were used for a dress shirt.

Point 5 ... soft and very good feeling    Point 4 ... soft and good feeling    Point 3 ... normal.    Point 2 ... stiff and feeling is bad.    Point 1 ... stiff and feeling is very bad.

The mark in the feeling column of the table shows; ◎ - average 4 to 5 points, ○ - average 3 to less than 4 points, △ - average 2 to less than 3 points, × - average 1 to less than 2 points.

(Table 6)

	Moisture absorbency (mg/m <sup>2</sup> )		feeling	frictional elect.voltage (V)
	Beginning	after washing		
Experiment 7	1800	1650	◎	220
Experiment 8	2050	1800	◎	180
Experiment 9	2400	1900	◎	250



(Table 7)

	Moisture absorbency (mg/m <sup>2</sup> )		feeling	frictional elect.voltage (V)
	Beginning	after washing		
Comparison16	600	500	○	1200
Comparison17	700	550	○	1050
Comparison18	550	450	○	950
Comparison19	1400	1100	×	360
Comparison20	150	—	○	6800

From table 6, it is understood that the amount of moisture absorbed in the treated taffeta cloth in experiments from 7 to 9 is high both at the beginning and after washing, showing that the taffeta has good moisture absorbency, because the taffeta is treated with a surface treatment chemicals containing a water soluble organic substance having an average molecular weight from 100 to 20000 and a reactive modifier. And the stuffy feeling of the treated taffeta cloth can be reduced when used for apparel. Especially, the taffeta of experiment 9 contains chitosan, shows remarkable improvement in moisture absorbency.

The feeling of the treated taffeta cloth of experiment 9 is soft and very good.

Moreover, the treated taffeta cloth of experiment 9 has a low frictional electrification voltage, showing that thus treated taffeta is material that gives little discomfort caused by static electricity.

The treated taffeta of experiment 8 where taffeta is treated by surface

treatment chemicals containing silk fibroin and collagen for water soluble organic substance, and compounds expressed by the chemical formulas 1 and 3 for reacting modifying agent, has more improved moisture absorbency and frictional electricity characteristics than the treated taffeta has in experiment 7.

5 From table 7, it is understood that the amount of moisture absorbed in the treated taffeta cloth in comparison 16 is low both at the beginning and after washing, showing that the taffeta is faulty in moisture absorbency, because the taffeta is treated with the surface treatment chemicals used in the experiment 1, which contains no water soluble organic substance. The taffeta has a high  
10 frictional electrification voltage, which shows thus treated taffeta is material that is apt to give discomfort resulting from static electricity.

The treated taffeta cloth in comparison 17 is treated with the surface treatment chemicals used in experiment 8 which has no water soluble organic substance, and has a low moisture pickup and a high frictional electrification  
15 voltage.

The treated taffeta cloth in comparison 18 is treated with the surface treatment chemicals used in experiment 9 which has no water soluble organic substance, and has a low moisture pickup and a high frictional electrification voltage.

20 The treated taffeta cloth in comparison 19 is treated with the surface treatment chemicals used in experiment 7 which contains a high molecular weight silk fibroin instead of a hydrolytic degradation product of silk fibroin, and is inferior in feeling.

The polyester cloth in comparison 20 is not treated and has a very  
25 small moisture pickup and a very high frictional electrification voltage.

( A fourth embodiment)

The surface treatment chemicals of the present embodiment correspond to the previously described fourth surface treatment chemicals and has the functional protein used in the second surface treatment chemicals and the reactive modifier used in the third surface treatment chemicals.

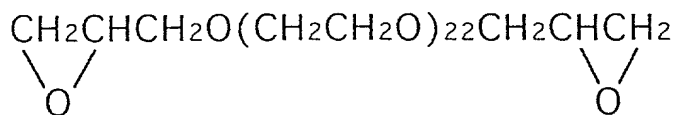
5 (Experiment 10)

A powder of whey protein and a hydrolytic degraded silk fibroin (weight distribution ratio 8:2) was diluted with water to make a 3.5% protein solution, and the pH of the solution was adjusted to 12 with sodium hydroxide. A chloroform solution of 2,4-toluene diisocyanate (TDI) was added to the protein solution and allowed to react at 45°C for two hours. After the reaction, the reacted liquid was kept for two hours at room temperature and separated into a water layer and a chloroform layer. Then the reacted liquid was filtered to be separated into the water layer and the chloroform layer. The pH of the water layer thus obtained was adjusted to 7, and the water layer was dried to obtain a functional protein powder.

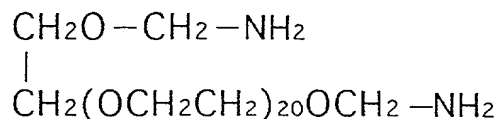
A concrete example of constituents and the concentration of the surface treatment chemicals were as follows.

	above described functional protein powder	..... 5 wt%
	a compound having the chemical formula 5	..... 4 wt%
20	a compound having the chemical formula 6	..... 3 wt%
	water	.....88 wt%

(Chemical formula 5)



(Chemical formula 6)



5        Using the surface treatment chemicals of the present experiment, polyester fibers (100 d / two folded yarn 48 filaments) was treated according to the following steps from ① to ⑥ written below and socks were made of thus treated yarn.

① The treated fiber was dyed in a cheese winding state and dried.

10        ② The dyed cheese wound fiber was put into Oba Myer dyeing machine and the surface treatment chemicals were applied at a bath ratio 1:20 to the fiber at 20°C for 20 minutes.

③ The treated fiber was dehydrated with a centrifugal dehydrator at a pick up rate 100%.

15        ④ The dehydrated fiber was put into a pressure vessel filled with moisture vapor and heated at 100°C for 20 minutes.

⑤ The heat treated fiber was washed and dried.

⑥ With a circular knitting hosiery machine, socks were made of the treated fiber.

20        (Comparison 21)

The fiber obtained from experiment 10 was dyed without any further treatment and socks were made in the same manner as in experiment 10.

(Evaluation of characteristics)

25        Moisture pickup, moisture absorbing speed, and frictional electrification voltage after washing were measured on the socks obtained in experiment 10 and comparison 21. The results are shown in Table 8.

The washing was carried out 50 times in conformity with JIS L-0217 Method 103.

The moisture absorbency was measured by; conditioning the moisture of sample by leaving in an atmosphere at 23°C, 30%RH for 12 hours, transferring into a room at 30°C, 80%RH and measuring change in weight between before and after moisture conditioning.

The moisture absorbing speed was determined by measuring time for a drop weighing about 40mg to be absorbed completely by being dropped from 3cm high on a pair of socks.

The frictional electrification voltage was measured based on JIS L-1094.

(Table 8)

	moisture pickup (%)		moisture absorbing speed (second)		Frictional electrification voltage (V)	
	beginning	after washing	beginning	after washing	Beginning	after washing
Experiment 10	2.2	2.0	< 1	< 1	200	680
Comparison 21	0.2	0.1	600 <	600 <	3400	5800

From table 8, it is found that the moisture pick up, moisture absorbing speed, and frictional electrification voltage are all good, since the socks of experiment 10 is made of the fiber treated with the fourth surface treatment chemicals.

## 5 Industrial Availability

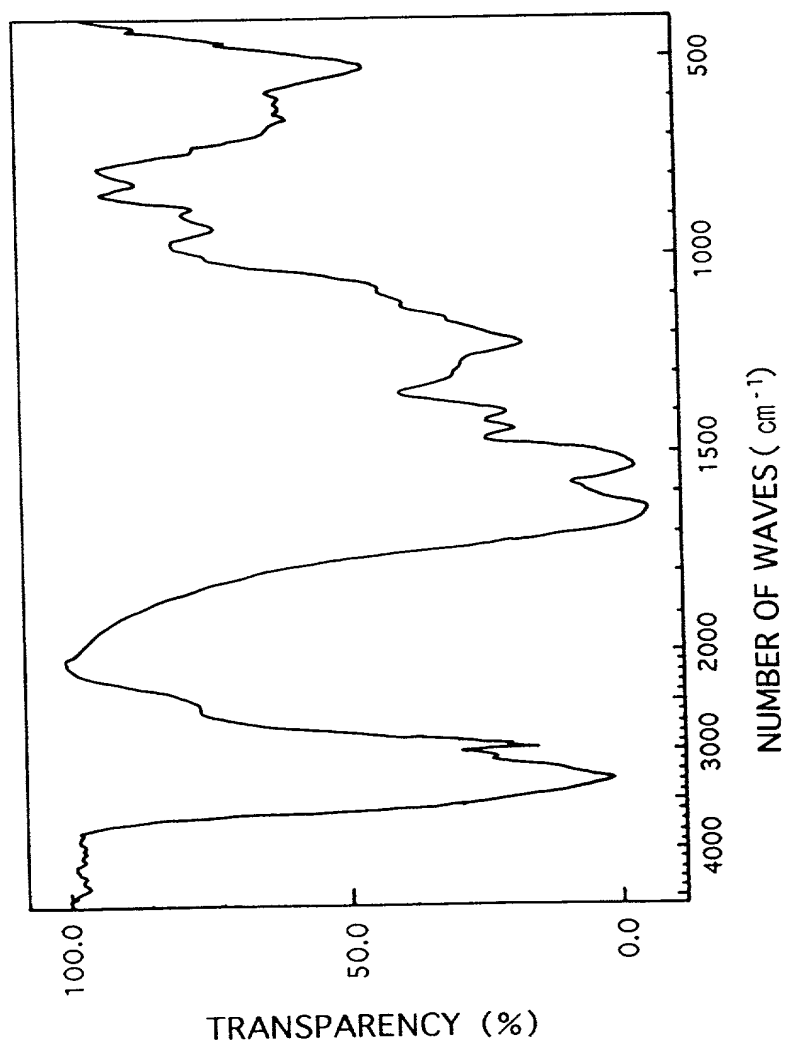
The present invention relates to surface treatment chemicals for improvement in hygroscopic-nonhygroscopic characteristics and is applicable as surface treatment chemicals for yarn, knitting, textiles and non-woven fabric.

## Abstract

A first fiber treatment comprising a functional protein prepared by treating proteins such as collagen with a cross-linking agent and a solvent-base resin; a second one comprising the above functional protein and a water-base resin; a third one comprising a water-soluble organic substance having an average molecular weight of 100 to 20000 and a reactive modifier; a fourth one comprising the above functional protein and a reactive modifier; and products such as fibers and textile goods treated with one of the treatments.

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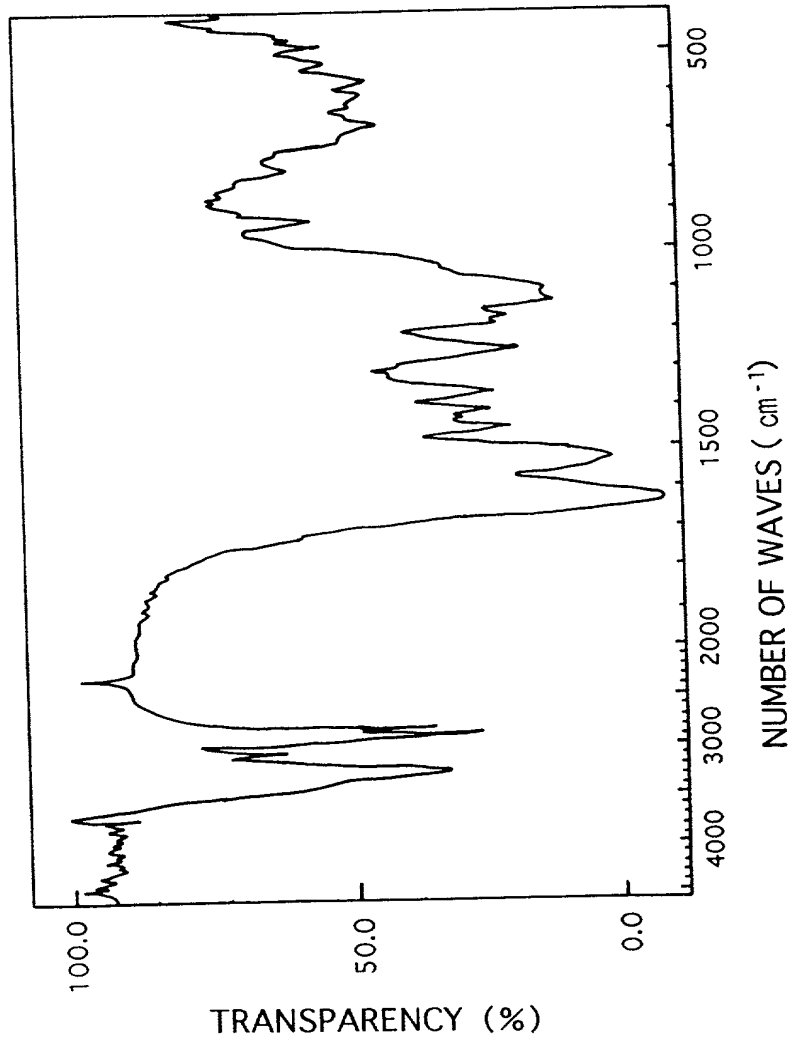
FIG. 1





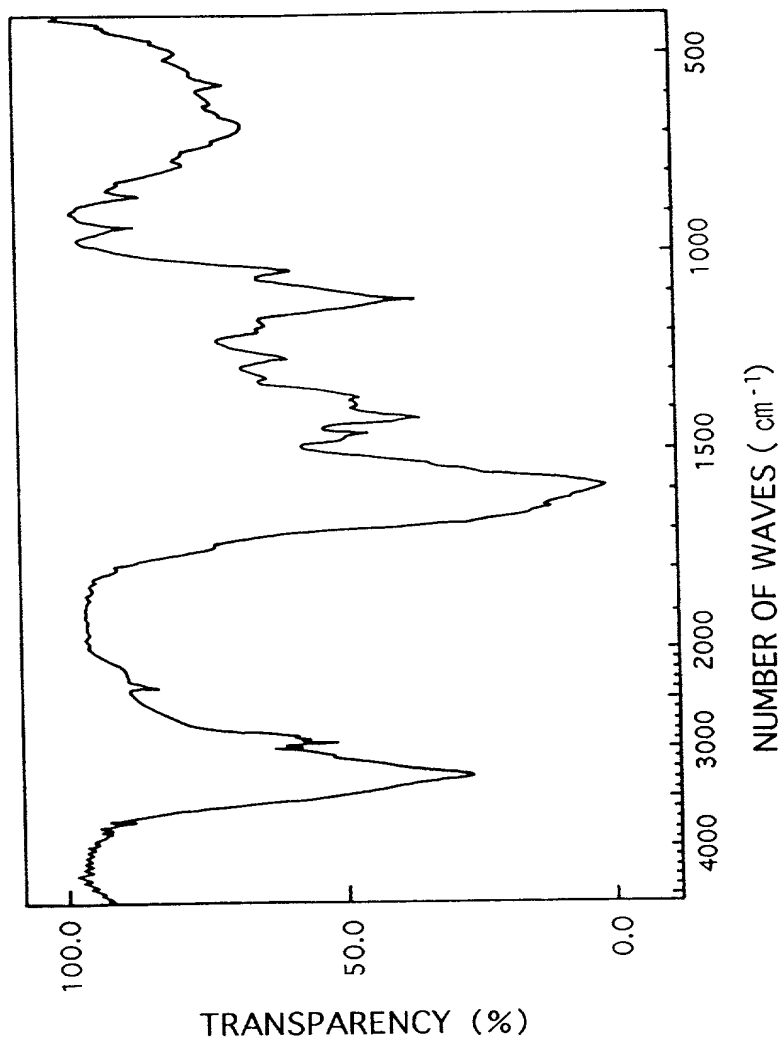
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FIG. 2



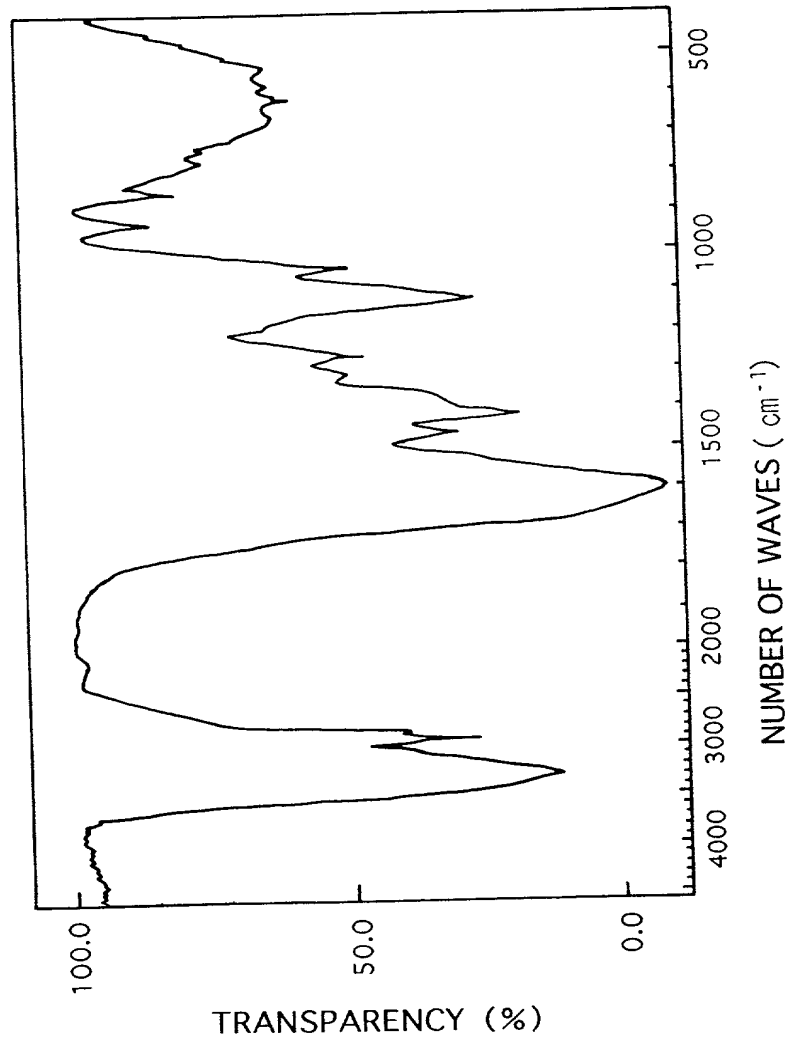
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FIG. 3



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FIG. 4



## Declaration and Power of Attorney For Patent Application

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

FIBER TREATMENT CHEMICALS, FIBER AND PRODUCT TREATED WITH THE FIBER TREATMENT

CHEMICALS

the specification of which (check one)

☐ is attached hereto.

☒ was filed on April 18, 1997 as Application Serial No. PCT/JP97/01350  
and was amended on November 17, 1997 (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above, to the best of my ability. I acknowledge the duty to disclose information which is material to the examination of this application in accordance with 37 C.F.R. 1.56(a) and 35 U.S.C. 102 and 103. I hereby claim foreign priority benefits under 35 U.S.C. 119/365 of any foreign application(s) for patent or inventor's certificate filed by me or my assignee disclosing the subject matter claimed in this application and having a filing date (1) before that of the application on which priority is claimed, or (2) if no priority claimed, before the filing date of this application:

Number	Prior foreign application(s)			Priority claimed	
	Country	Day/Month/Year Filed	Yes	No	
[ 8-98760 ]	[ Japan ]	[ 19/04/1996 ]	[ X ]	[ ]	
[ 8-98761 ]	[ Japan ]	[ 19/04/1996 ]	[ X ]	[ ]	
[ 8-183725 ]	[ Japan ]	[ 12/07/1996 ]	[ X ]	[ ]	
[ ]	[ ]	[ ]	[ ]	[ ]	
[ ]	[ ]	[ ]	[ ]	[ ]	
[ ]	[ ]	[ ]	[ ]	[ ]	
[ ]	[ ]	[ ]	[ ]	[ ]	

I hereby claim the benefit under 35 U.S.C. 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of 37 C.F.R. 1.56 (a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Application Serial No.	Filing Date	Status(patented, pending, abandoned)
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Application Serial No.	Filing Date	Status(patented, pending, abandoned)
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Application Serial No.	Filing Date	Status(patented, pending, abandoned)
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Application Serial No.	Filing Date	Status(patented, pending, abandoned)
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I hereby declare that all statement made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint Flynn, Thiel, Boutell & Tanis, P.C., 2026 Rambling Road, Kalamazoo, Michigan 49008-1699, telephone number 616-381-1156 (to whom all communications are to be directed), and the below named partners thereof (of the same address) individually and collectively my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent, and I hereby authorize them to act and rely on instructions from and communicate directly with the person/assignee/attorney/ firm/organization who/which first sends/sent this case to them and by whom/which I hereby declare that I have consented after full disclosure to be represented unless/until I instruct Flynn, Thiel, Boutell & Tanis, P.C. in writing to the contrary.

8-  
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